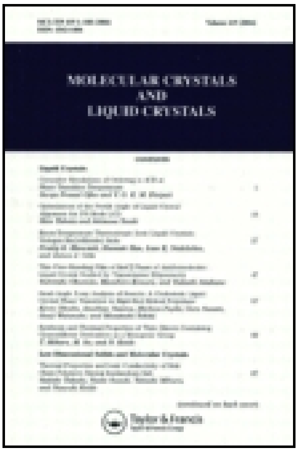


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Goldstone Mode Relaxation in the Ferroelectric Phases of 8OSI

M. Pfeiffer [a], S. Wrobel [a b], L. A. Beresnev [a c] & W. Haase [a]

[a] Institut fur Physikalische Chemie, TH-Darmstadt, Petersenstr. 20, D-6100, Darmstadt, FRG

[b] Institute of Physics, Jagellonian University, Reymonta 4, 30-059, Kraków, Poland

[c] Institute of Crystallography, USSR Acad. Sci., Leninsky Prosp. 59, 117333, Moscow, USSR

To cite this article: M. Pfeiffer, S. Wrobel, L. A. Beresnev & W. Haase (1991): Goldstone Mode Relaxation in the Ferroelectric Phases of 8OSI, Molecular Crystals and Liquid Crystals, 202:1, 193-206

To link to this article: http://dx.doi.org/10.1080/00268949108035670

Mol. Cryst. Liq. Cryst., 1991, Vol. 202, pp. 193–206
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Goldstone Mode Relaxation in the Ferroelectric Phases of 8OSI

M. PFEIFFER, S. WROBEL,† L. A. BERESNEV‡ and W. HAASE
Institut für Physikalische Chemie, TH-Darmstadt, Petersenstr. 20, D-6100 Darmstadt, FRG

(Received September 14, 1990)

The ferroelectric properties of the Sm C*, Sm I*, Sm J* and Sm K* phases of 4-(2-methylbutyl)-phenyl-4′-(octyloxy)-(1,1′)-biphenyl-carboxylate (8OSI) have been studied by dielectric spectroscopy. We observed the bias field dependence of the Goldstone mode and a weak low frequency molecular relaxation. The Sm C* and Sm I* phases showed a composed absorption peak with a critical frequency of ca. 1 kHz. In the highly ordered Sm J* phase there is only a weak absorption peak at about 0.8 kHz. In the Sm K* phase no Goldstone mode has been detected, but only a contribution coming from a molecular relaxation process. The Goldstone mode could be suppressed by an electrical field of about 30 kV/cm. The study of the Goldstone mode was performed in the presence of an aligning magnetic field of 1.2 T parallel to the helix and also without magnetic field. It was found that a magnetic field of 1.2 T is sufficient to reduce the Goldstone mode dielectric increment by about 50%. The fits of the Cole-Cole function to the dielectric spectrum allowed us to calculate the dielectric increments and the critical frequencies of the Goldstone mode and of the molecular relaxation process. The critical frequency of the Goldstone mode increases with the bias field, but it is practically temperature independent within one ferroelectric phase. This increase is discussed in terms of elastic moduli and rotational viscosity. The critical frequency of the molecular process obeys an Arrhenius law with an activation energy of (119 ± 15) kJ/mole in the Sm C* and Sm I* phases.

INTRODUCTION

Ferroelectrtic liquid crystals are novel materials promising very interesting applications in science and technology. In tilted smectic phases (Sm C, Sm I, Sm F and so on) composed of rod like molecules the local point symmetry is *2/m*. This does not allow for spontaneous polarization to occur. In the case of chiral molecules the local symmetry is broken to *2*. When in addition the molecules are polar, a spontaneous in-plane polarization ($\mathbf{P}_\perp$) shows up parallel to the *2*-fold symmetry axis. However, due to the chirality of the molecules the symmetry axis turns its direction going from one layer to another. This leads to a helicoidal order of the in-plane *2*-fold axis and the in-plane polarization as well.

The effect of ferroelectricity in tilted smectic phases was theoretically predicted by R. B. Meyer and found experimentally in DOBAMBC.[1] This substance has

---

† Permanent addresses: Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Kraków, Poland.

‡ Institute of Crystallography, USSR Acad. Sci., Leninsky Prosp. 59, 117333 Moscow, USSR.

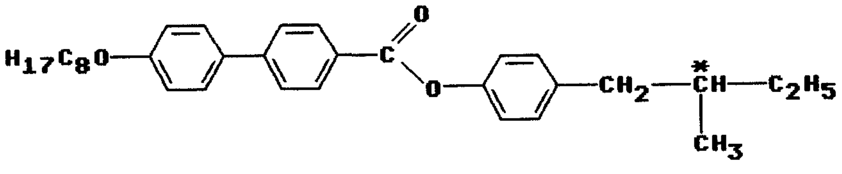
been thoroughly studied by different groups.[2-4] It was established that ferroelectric liquid crystals behave more or less in the same way as classical ferroelectrics. For instance, they exhibit a soft mode relaxation in the vicinity of the Sm A* – Sm C* transition. The dielectric increment for this relaxation obeys a Curie-Weiss law.

Ferroelectricity in tilted smectic phases was also found for mixtures consisting of achiral molecules doped with a chiral component.[5] Some of the mixtures are very important from the application point of view, however, the interpretation of the results is rather difficult.[6,7] Due to this fact in this paper we are dealing with a single component system (8OSI) which shows a weak spontaneous polarization. Its polymorphism is very rich: the substance exhibits at least three different ferroelectric phases: Sm C*, Sm I* and Sm J*. The aim of our work is to study the low frequency dielectric spectrum of 8OSI in different phases as a function of the bias field. Our preliminary results obtained for 8OSI on 25 μm and 12 μm thick samples were published recently.[8,9]

EXPERIMENTAL

Material

4-(2-methylbutyl)phenyl-4′-(octyloxy)-(1,1′)-biphenyl-4-carboxylate (8OSI) has the following structural formula:



It is a liquid crystalline substance with the following phase diagram:

I-171.8-BP-171.7-Ch-170.2-Sm A*-130.5-Sm C*-79.7-Sm I*-73.3-Sm J*-61.9-Sm K*,

(temperatures in °C). Due to the chirality of its molecules it exhibits a blue phase (BP) and three ferroelectric liquid crystalline phases: Sm C*, Sm I* and Sm J*. According to our preliminary measurements[8,9] the Sm K* phase shows no ferroelectric behavior due to some strong intermolecular correlations.

Methods

To take the dielectric spectra of the liquid crystalline phases of 8OSI a Hewlett-Packard 4192 A impedance analyzer controlled by an ATARI Mega 2 computer was used. New programmes and subroutines[10] allowed us to take up to 100 experimental points per power of ten Hertz and to process the data immediately after the acquisition process. The quality of the data was controlled by graphic programs. The fits of the Cole-Cole functions were done using an IBM 3090 computer.

Our preliminary dielectric measurements on 8OSI[8,9] revealed that this substance exhibits rather weak ferroelectric properties in the Sm C* and Sm I* phases. In the Sm J* phase the effect observed was very small.[8] Using the 25 μm thick sample it was not possible to suppress the Goldstone mode completely by applying the bias fields available with the HP bridge. In this paper we report the measurements done for 12 μm thick samples using both gold coated and ITO electrodes.

The alignment of the samples was obtained by slow cooling from the isotropic phase to the Sm C* phase in the presence of a magnetic field of 1.2 T ($\mathbf{B}_o \parallel \mathbf{k}$, $\mathbf{E} \parallel x$), where **k** is the wave vector of the helix and (x, y, z) is the laboratory framework, the z-axis of which coincides with the helix axis ($\mathbf{k} \parallel z$). Before measurement of the Goldstone mode, the helix which had partially been suppressed by the aligning magnetic field was recovered by applying an AC-voltage with decreasing amplitude.

Dielectric Spectra in the Sm C* and Sm I* Phases of 8OSI

The dielectric spectra obtained for the Sm C* phase of 8OSI are presented in Figures 1 and 2 in the form of absorption ($\varepsilon''_\perp(\nu)$) and dispersion ($\varepsilon'_\perp(\nu)$) curves. In both cases a broad absorption peak appears in the frequency range between 100 Hz and 1 MHz. These absorption spectra consist of, at least, two contributions: the Goldstone mode relaxation centered at about 10^3 Hz and a higher frequency relaxation with the critical frequency of 10^5 Hz. The second process results in a shoulder on the high frequency side of the composed absorption peak (Figure 2). It can be noticed that the Goldstone mode is strongly bias field dependent and it practially disappears at the highest applied fields. However, the critical fields are in this case very high because the spontaneous polarization is rather weak and the pitch of the helix is very short. The critical frequency of the Goldstone mode increases with the bias field.

The measurements were done also in the presence of an aligning magnetic field (Figure 2), which was parallel to the helix axis ($\mathbf{B}_o \parallel \mathbf{k} = (2\pi/p_o)z$) and perpendicular to the measuring electric field ($\mathbf{E} \perp \mathbf{B}_o$). p_o is the helical pitch. The magnetic field influences the spectrum in two ways. First it reduces the intensity of the dielectric spectrum by a factor of about 2 and second it shifts the whole spectrum to higher frequencies. The first effect was observed for DOBAMBC[11] but at fields between 4T and 8T. There are at least three reasons which explain the smaller critical magnetic field for 8OSI than for DOBAMBC.

1) Differences in the molecular structure; 8OSI has a three ring system with higher diamagnetic anisotropy.
2) In the case of 8OSI the Sm C* temperature range falls within higher temperatures than that of DOBAMBC. This is an indication that the twist viscosity is smaller for 8OSI and that it is easier to move the molecule's long axis around the cone's surface.
3) The experiment on DOBAMBC[11] was done in a magnetic field being perpendicular to the helix axis.

The high frequency process is practically insensitive to the bias field. Most probably, the reasons for this come from the low frequency molecular relaxation connected with the reorientation of the molecules around their short molecular axes,

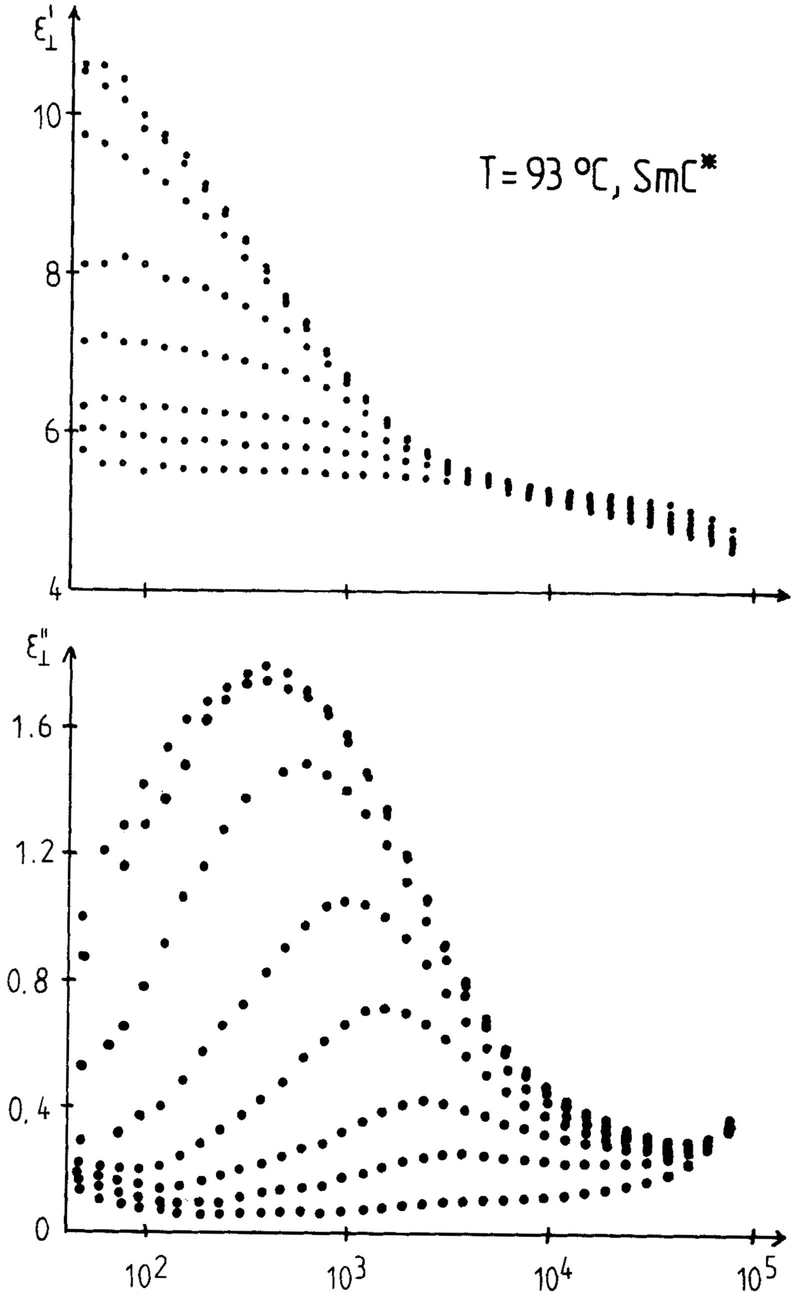


FIGURE 1 Dielectric spectra (real (ε') and imaginary (ε") part of the electric permittivity) showing the Goldstone mode and a weak molecular relaxation in the SmC* phase at different bias fields. The spectra were taken in absence of the magnetic field. Cell thickness = 11 μm. The bias voltages are (from top to bottom): 0, 3, 6, 9, 15, 24, 30, 33 V.

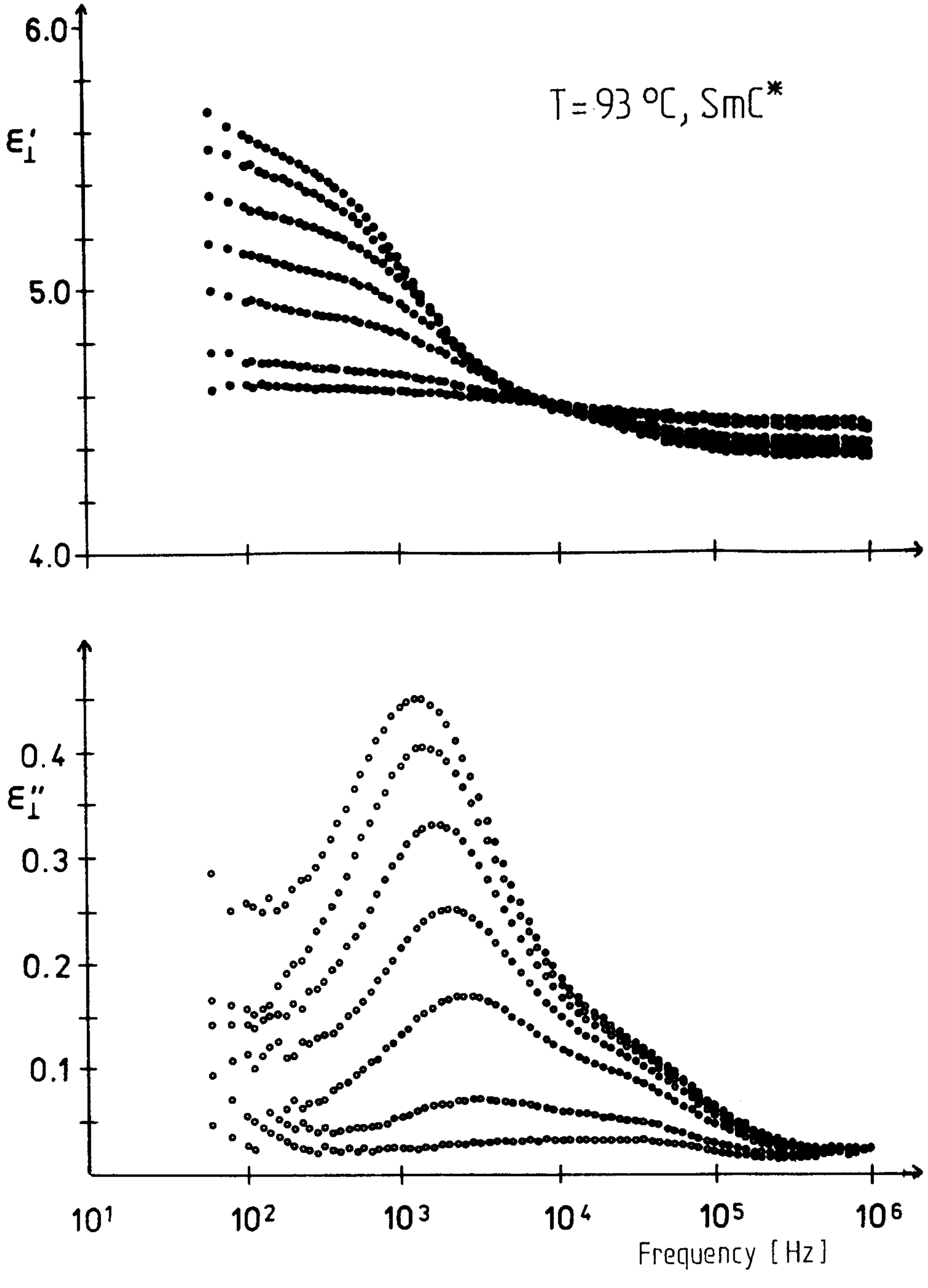


FIGURE 2 Dielectric spectra (real (ε') and imaginary (ε") part of the electric permittivity) showing the Goldstone mode in the SmC* phase at different bias fields in the presence of a magnetic field of 1.2 T. The molecular relaxation appears clearly due to the partially suppressed Goldstone mode. Cell thickness = 11 μm. The bias voltages are (from top to bottom): 0, 5, 10, 15, 20, 25, 30 V.

i.e. 2-fold symmetry axis. Unlike other systems,[2-4,6,7,12] even very close to the Sm A* – Sm C* transition, no soft mode could be found. This effect can be explained by the weakness of the lateral dipole moment of 8OSI and the decoupling of the dipolar group and the chiral center. Experiments on a similar compound CE8 could not detect a soft mode either.[13] Figure 3 presents the dielectric spectra for the Sm I* phase obtained at different bias fields. The Goldstone mode relaxation is also present here and exhibits a lower intensity.

DISCUSSION

Analysis of the Dielectric Spectrum

The dielectric spectrum observed in the Sm C* and Sm I* phases is rather complex. It was found that the sum of two Cole-Cole functions:

$$\varepsilon_{\perp}^{*} = \varepsilon_{\perp}' - i\varepsilon_{\perp}'' = \varepsilon_{\perp\infty} + \frac{\Delta\varepsilon_M}{1 + i(\omega\tau_M)^{1-\alpha_M}} + \frac{\Delta\varepsilon_G}{1 + i(\omega\tau_G)^{1-\alpha_G}} \tag{1}$$

gives the best fits to the experimental points. In Equation (1) $\Delta\varepsilon_M$ and $\Delta\varepsilon_G$ are the dielectric increments due to the molecular relaxation and the Goldstone mode. $\varepsilon_{\perp\infty}$ is the high frequency electric permittivity coming from the induced polarization (electronic and atomic) and from the high frequency molecular processes, i.e., the reorientation around the long molecular axis as well as the stochastic precession. In other words $\varepsilon_{\perp\infty}$ is the dielectric permittivity measured in the Sm A* phase far from T_c.[14] τ_M and τ_G are the molecular and the Goldstone mode relaxation times respectively, and α_M and α_G are the respective distribution parameters.

Figure 4 shows the fits of two Cole-Cole dispersion and absorption curves to the experimental points obtained at different bias fields. The solid lines are calculated assuming the two relaxation mechanisms. In the region below 100 Hz the effective absorption curve goes to infinity due to the conductivity effect. It can be seen that the position of the absorption peak connected with the molecular process does not change on the frequency scale upon increasing the bias field. On the other hand the Goldstone mode absorption peak shifts to higher frequencies as the bias field increases.

It is interesting to point out that the Goldstone mode absorption peak has a symmetric distribution of the relaxation times ($\alpha_G \approx 0.08$) and its critical frequency is practically temperature independent within a given phase. In this sense our results agree very well with those obtained by Cava, Patel and Rietman for CE8.[13]

The molecular process shows a narrow distribution of the relaxation times ($\alpha_M \approx 0$). As mentioned before this process is most probably connected with the reorientation of the molecules around their short axes. The activation energy computed for this process using the Arrhenius equation gives a value of (119 ± 15) kJ/mol, which is typical for the low frequency molecular relaxation.

Bias Field Dependence of the Goldstone Mode

The bias field dependence of the Goldstone mode dielectric strength $\Delta\varepsilon_G = \varepsilon_o - \varepsilon_\infty$ (Figure 5) shows the usual behaviour.[2-4,11,14] It is suppressed by the external

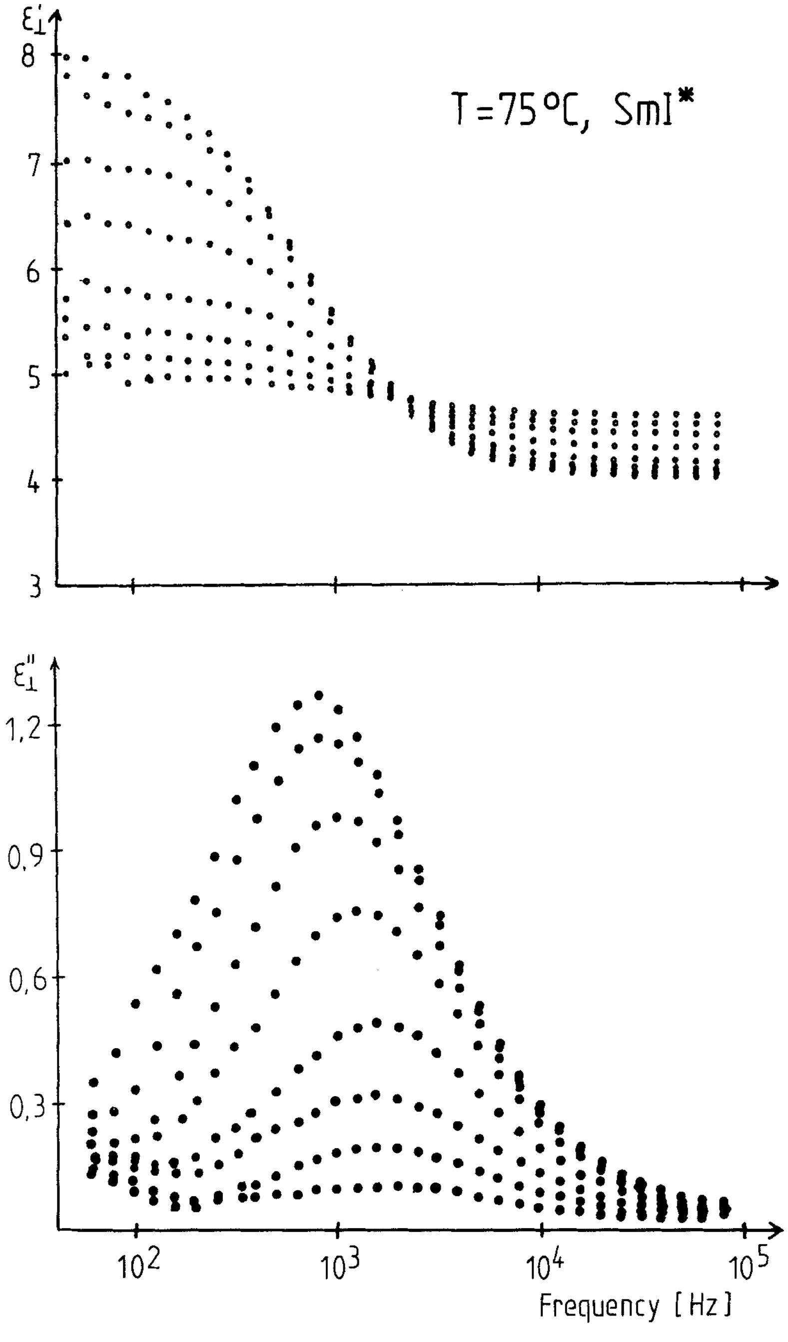


FIGURE 3 Dielectric spectra (real (ε') and imaginary (ε'') part of the electric permittivity) showing the Goldstone mode in the SmI* phase at different bias fields. The molecular relaxation is covered by the Goldstone mode. The spectra were taken in the absence of the magnetic field. Cell thickness = 11 μm. The bias voltages are (from top to bottom): 0, 5, 11, 18, 26, 28, 30, 33 V.

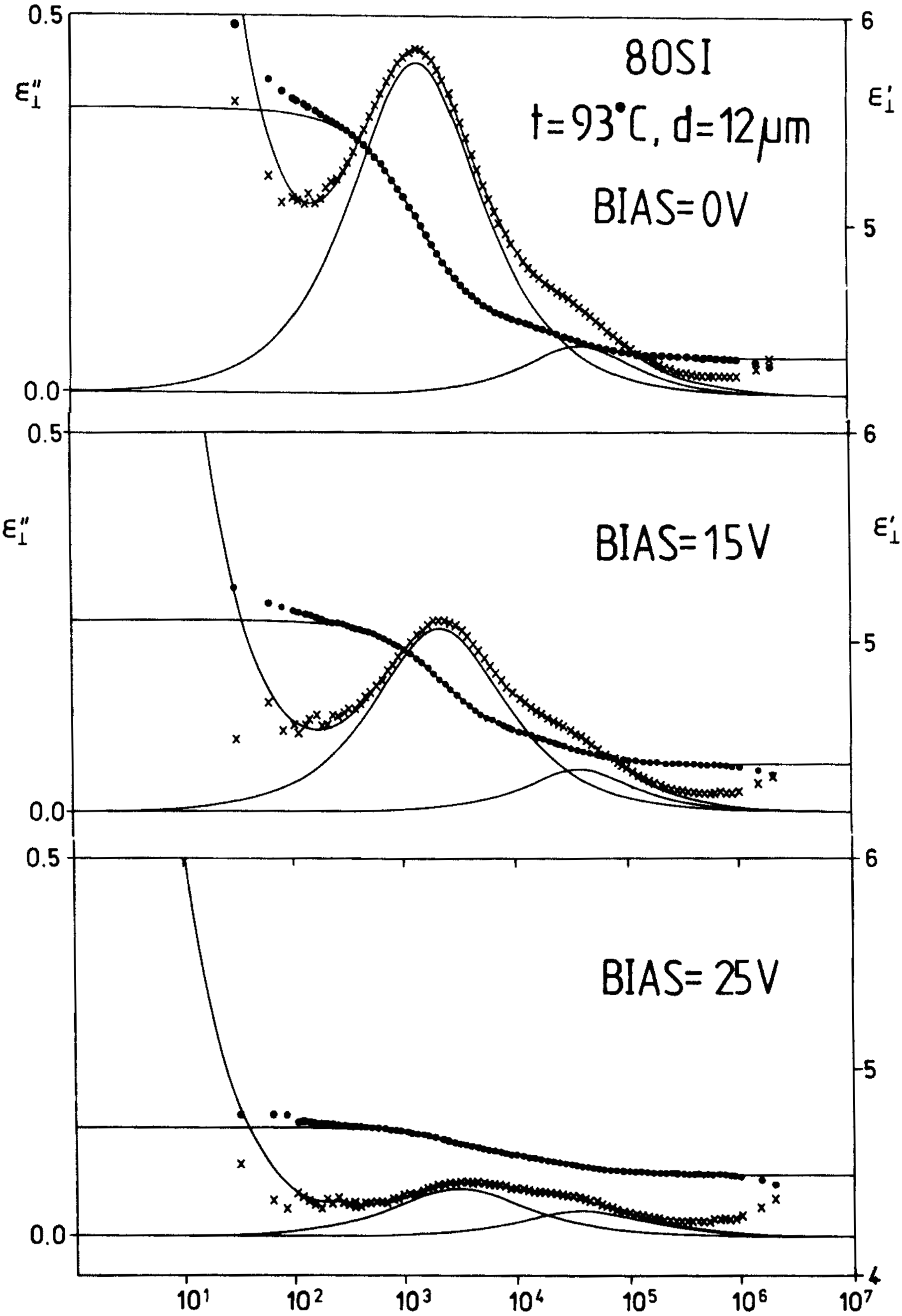


FIGURE 4 Separation of the Goldstone mode and the molecular mode. The lines are fits using two Cole-Cole functions, taking the sample conductivity into account at low frequencies. The Goldstone mode shows only a slightly broadened relaxation time distribution.

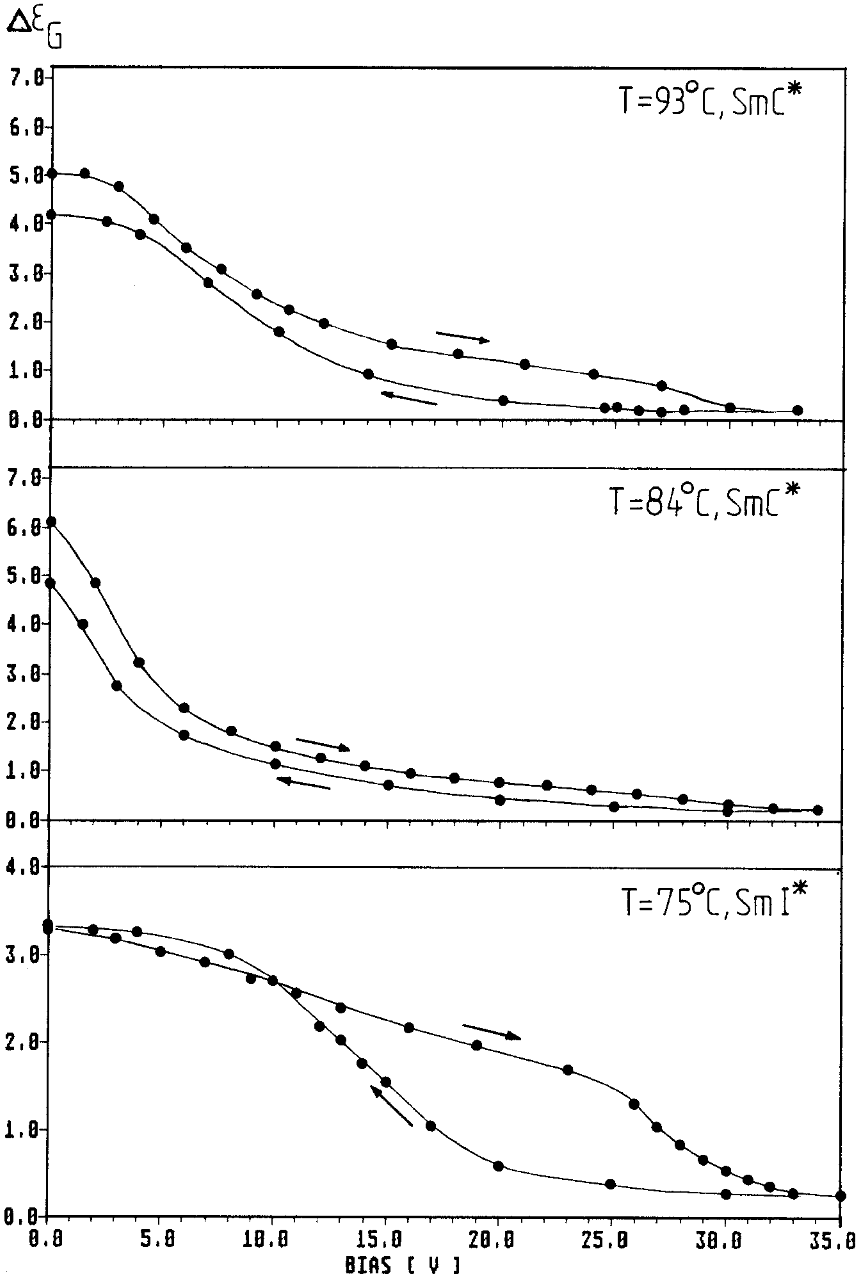


FIGURE 5 The relaxation strength of the Goldstone mode as a function of bias field displays the suppression of the Goldstone mode with increasing voltage. A decrease of the voltage leads to hysteresis. The range where the helix is deformed and where it collapses can be seen.

field due to the process of unwinding which results in the total disappearence of the helix. However, the dielectric increment[4,11,12] does not obey an $E^{-2/3}$ law established for classical and liquid crystalline ferroelectrics as well.[12] Hysteresis of $\Delta\varepsilon_G(V)$ is observed, which is connected with the difference between the voltage V_u of the disappearance of the helix, accompanied by a disappearance of the dechiralization lines, and the voltage V_w of the reappearance of them.[15] The more pronounced hysteresis is observed in the SmI* phase due to a larger viscosity of this phase.

The most interesting result, in our opinion, is the drastical increase of the critical frequency ν_R of the Goldstone mode with an increase of the bias field (Figure 6).[16] The values of ν_R have been found by fitting Equation 1 to the experimental points (Figures 1–3). The physical nature of such behaviour of the Goldstone mode characteristic frequency has not yet been discussed, though it was pointed out[13] that this increase is probably due to the shift of oscillator strength to higher frequency, than to the elimination of low frequency modes when the bias field is applied.

Here we analyze the behaviour of the Goldstone mode on the basis of the assumption, that the critical frequency ν_R measured by dielectric spectroscopy has the same physical nature as a characteristic frequency of an electrooptical response of helical FLC under a weak a.c. field (deformed helix ferroelectric (DHF)-effect).[17] Then the following Equation may be used:

$$\nu_R \sim \frac{K\,\Theta_o^2}{\gamma_\varphi p_o^2} \tag{2}$$

where K is the effective elastic modulus, γ_φ is the rotational viscosity and Θ_o is the molecular tilt angle.

The bias field dependence of the value of the helical pitch p_o has theoretically been predicted,[17,18] however the absolute change of p_o due to the bias field is rather small, and moreover because of the increase of the p_o with voltage the ν_R has to decrease. This is contrary to our observations.

Therefore we believe that the increase of ν_R with bias voltage could be connected with the increase of the effective value of elastic modulus K in Equation (2). For a more detailed discussion we refer to Figure 7. Without any bias field the "classical" helicoidal structure takes place. Moving along the z-axis (normal to smectic layers) the molecular tilt plane rotates uniformly, and the dependence of the azimuthal angle $\varphi(z)$ can be described as

$$\varphi(z) = \sin(2\pi z/p_o). \tag{3}$$

A weak bias field induces a helix deformation, which could be described as a deviation of the curve $\varphi(z)$ from the sine-wave form.[18] (see Figure 7c, d). It is clear, that the larger the value of the bias voltage, the larger the area of the sample (or a part of the helix along the z-axis), where uniform states take place (here uniform states are the states of the molecular director $\vec{n}$ being parallel to the planes of the electrodes[19] (positions A in Figure 7a)). These uniformly oriented states do

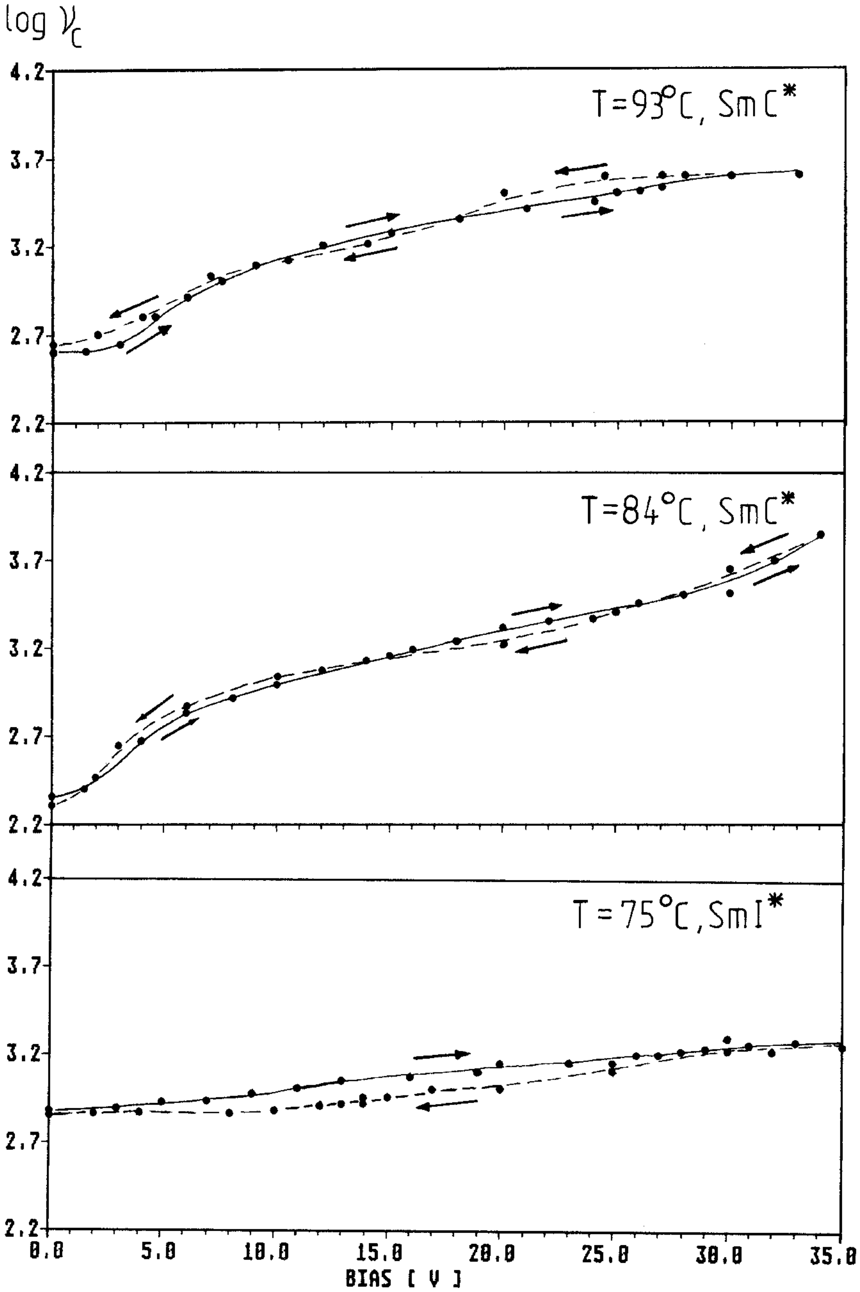


FIGURE 6 Bias dependence of the Goldstone mode critical frequency. The increase of the relaxation frequency can be explained with a change in the elasticity of the helix (see text).

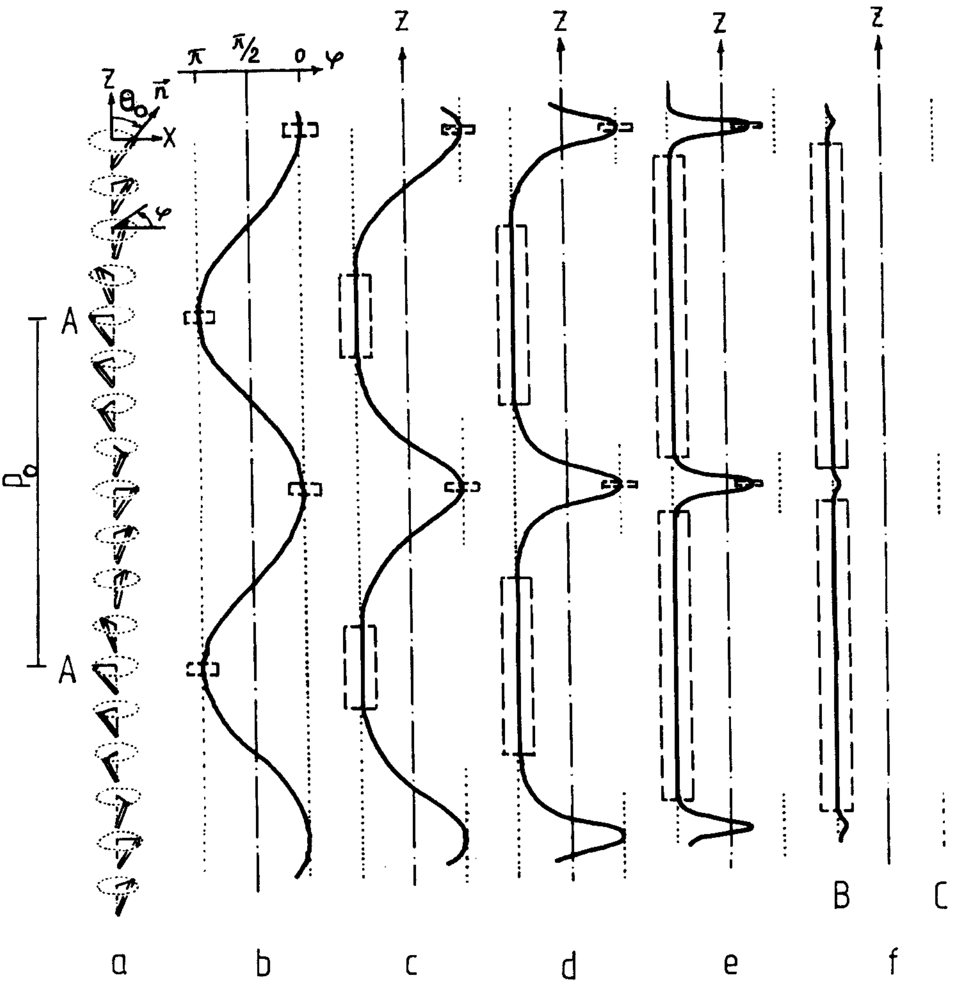


FIGURE 7 The deformation of the helix due to an external electric field - the suppression of the Goldstone mode. [a,b] The distribution of the azimuthal angle φ of the tilt plane in undisturbed helical ferroelectric liquid crystal. [c,d,e,f] The bias field (perpendicular to the picture plane) increases. [d,e] Transition is accompanied with the motion of the dechiralisation lines. [f] Uniform state (B) at given polarity of bias. At the opposite polarity the other uniform state (C) takes place. The areas with suppressed Goldstone mode are marked with rectangles.

not give any contribution to the Goldstone mode.[20] Therefore the absolute value of the dielectric permittivity (both ε′ and ε″) should decrease due to the fact that the remaining non-uniformly oriented parts of the sample area are decreasing (see Figure 7c–e).

At the same time in these non-uniformly oriented areas the helix deformation increases (due to twist and bend deformations), and because of this an increase of the elastic modulus should take place. This is similar to a string which increases its elasticity under increasing deformation. In both cases (FLC and string) an increase of the characteristic frequency should be observed.

The critical frequency (ν_R) of the Goldstone mode found in our dielectric spectroscopy experiments, as we have defined it above (Equation 2), is analogous to the characteristic frequency of electro-optical response. Therefore this phenomenon has to manifest in electro-optical experiments. Indeed, detailed analyses of oscillograms reported by Beresnev *et al.*[21] give us an appreciable decrease of the rise and decay times of the electro-optical response of DHF-effect when increasing the amplitude of meander voltage.[22]

A relatively weaker dependence of the critical frequency on the bias field is observed in the SmI* phase in comparison with the SmC* phase. We suggest that due to some kind of intermolecular correlations of the neighbouring smectic layers in the SmI* phase the latter possesses higher plasticity than the SmC* phase.[23] If the helix deformation exceeds some critical value the elastic moduli (first of all for twist deformation) increases not so strongly due to the irreversibility of the deformation process. Using the "string analogy" this case corresponds to a more "plastical" string. Of course, at weak bias or without it the characteristic frequency could be higher than in the SmC* phase, as it happens in our experiment, check for instance, the relaxation frequencies at 84° and 75°C at zero bias (Figure 6).

It should be noted that after total unwinding of the helix in a strong d.c. field, it is possible to observe the molecular mode at frequencies of about 10^5–10^6 Hz, connected with the usual reorientations of molecules around their short axes[24] (Figure 4). Besides this in FLCs with high spontaneous polarization a new ferroelectric mode is observed[25] in the interval 10^4 Hz, which is, probably, connected with the formation of ferroelectric domains recently discovered.[26]

CONCLUSIONS

A, The Goldstone mode relaxation found for the Sm C* and Sm I* phases of 8OSI shows up at higher frequencies than for DOBAMC[2] and some other room temperature ferroelectric mixtures.[4,6] B, The Goldstone mode relaxation spectrum is strongly bias field dependent. C, In the presence of an aligning magnetic field the Goldstone mode is strongly suppressed and the effectiveness of the helix distortion is in the case of 8OSI much higher than for DOBAMBC. This is an important point for NMR experiments using higher fields (given by superconducting magnets) at which the helix is completely unwounded.

Acknowledgments

The authors are thankful to E. Merck Company for 8OSI samples obtained as a gift. S.W. would like to thank the WE-Heraeus-foundation for the invitation and financial support.

References

1. R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller, *J. Phys. Lett. (Paris)*, **36**, L69, (1975).
2. B. I. Ostrovski, A. Z. Rabinowicz, A. S. Sonin and B. A. Strukov, *Zh. Eksp. Ter. Fiz.*, **74**, 1448, (1978).

3. J. Hoffmann, W. Kuczynski and J. Malecki, *Mol. Cryst. Liq. Cryst.*, **44**, 287, (1978).
4. M. Glogarova, J. Fousek, L. Lejcek and J. Pavel, *Ferroelectrics*, **55**, 117, (1984).
5. K. Siemensmeyer and H. Stegemeyer, *Chem. Phys. Lett.*, **148**, 409, (1988).
6. A. M. Biradar, S. Wrobel and W. Haase, *Phys. Rev.*, **A39**, 2693, (1989).
7. S. Wrobel, A. M. Biradar and W. Haase, *Ferroelectrics*, **100**, 271, (1989).
8. S. Wrobel, M. Pfeiffer, A. M. Biradar and W. Haase, *MRS Symp. Proc.*, Vol. 173, "Advanced Organic Solid State Material," L. Y. Chiang, P. M. Chaikin and D. O. Cowan (eds.), p. 525, Pittsburgh, 1990.
9. W. Haase, S. Wrobel and M. Pfeiffer, *SPIE Proc.*, Vol. 1257, "Liquid Crystal Displays and Applications," J. W. Doane and Z. Yaniv (eds.), p. 104, Bellingham, 1990.
10. M. Pfeiffer and W. Haase, unpublished results.
11. I. Musevic, B. Zeks, R. Blinc, Th. Rasing and P. Wyder, *Phys. Stat. Sol.* (*b*), **119**, 727, (1983).
12. M. Glogarova and J. Pavel, *Liquid Crystals*, **6**, 325, (1989).
13. R. J. Cava, J. S. Patel and E. A. Rietman, *J. Appl. Phys.*, **60**, 3093, (1986).
14. J. P. Parneix and C. Legrand, *Ferroelectrics*, **84**, 199, (1988).
15. S. Dumrongrattana and C. C. Huang, *J. Physique*, **47**, 2117, (1986).
16. S. U. Valerien, F. Kremer, H. Kapitza, R. Zentel and W. Frank, *Physics Letters A*, **138**, 219, (1989).
17. L. A. Beresnev, V. G. Chigrinov, D. I. Dergachev, E. P. Pozhidayev, J. Fünfschilling and M. Schadt, *Liquid Crystals*, **5**, 1171 (1989).
18. B. I. Ostrovski, A. Z. Rabinovich and V. G. Chigronov, "Advances in Liquid Crystal Research and Applications," ed. by L. Bata, p. 469, Pergamon Press - Akad. Kiado, Budapest, 1980.
19. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
20. See Reference 5 and References 2, 3, 5, 7, 10–14 therein.
21. L. A. Beresnev, L. M. Blinov and D. I. Dergachev, *Ferroelectrics*, **85**, 173, (1988).
22. E. P. Pozhidayev, *et al.* to be published.
23. J. Doucet, P. Keller, A. M. Levelut and P. Porquet, *J. Physique*, **39**, 548, (1978).
24. A. M. Biradar, S. Wrobel and W. Haase, *Phys. Rev. A*, **39**, 2693, (1989).
25. L. A. Beresnev, M. Pfeiffer, W. Haase, M. V. Loseva and N. I. Chernova, to be published.
26. L. A. Beresnev, M. V. Loseva, N. I. Chernova, S. G. Kononov, P. V. Adomenas and E. P Pozhidayev, *Pis' ma Zh. Eksp. Teor. Fiz.*, **51**, 457, (1990).